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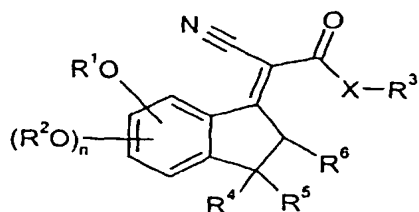
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(54) Novel indanylidene compounds

(57) The invention relates to novel indanylidene compounds which are effective in absorbing ultra violet radiation and to light screening compositions comprising said indanylidene compounds of the general formula



R³ signifies C₁-C₂₀ alkyl, C₂-C₂₀ alkyl in which at least one methylene group is replaced by oxygen, C₃-C₂₀ alkenyl, C₃-C₂₀ alkynyl or a group YS;

R⁴, R⁵, R⁶ each independently signify H or C₁-C₂₀ alkyl;

n signifies 0, 1 or 2;

Y signifies a linker group;

S signifies a silane-, an oligosiloxane- or a polysiloxane-moiety;

with the proviso that at least one of the residues R¹, R² or R³ signifies YS.

wherein

X signifies O or NH;

R¹ signifies C₁-C₂₀ alkyl, C₂-C₂₀ alkyl in which at least one methylene group is replaced by oxygen, C₃-C₂₀ alkenyl, C₃-C₂₀ alkynyl or a group YS;

R² signifies C₁-C₂₀ alkyl, C₂-C₂₀ alkyl in which at least one methylene group is replaced by oxygen, C₃-C₂₀ alkenyl, C₃-C₂₀ alkynyl or a group YS; or R¹ and R² can combine on adjacent C-atoms to form a dioxomethylene ring;

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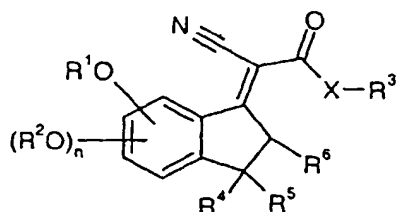
Description

[0001] The invention relates to novel indanylidene compounds which are effective in absorbing ultra violet radiation and to light screening compositions comprising said indanylidene compounds.

[0002] Light screening compositions comprising indanylidene compounds are described in the European patent publication EP 0823 418 A2. This publication especially refers to cyano-(2,3-dihydroxy-1H-inden-1-ylidene) acetic acid ester compounds. These compounds do not have a sufficient solubility in the media usually employed in cosmetics, in particular in oil and fats. Furthermore, it is desirable that the active ingredient remain on the surface of the skin rather than penetrate into or through the skin.

[0003] It has now been found that compounds having an indanylidene residue grafted via a linker to a silane, an oligosiloxane- or a polysiloxane moiety overcome the problem of penetration and show improved solubility.

[0004] According to this invention there are provided compounds of the general formula I



wherein

X signifies O or NH;

R¹ signifies C₁-C₂₀ alkyl, C₂-C₂₀ alkyl in which at least one methylene group is replaced by oxygen, C₃-C₂₀ alkenyl, C₃-C₂₀ alkynyl or a group YS;

R² signifies C₁-C₂₀ alkyl, C₂-C₂₀ alkyl in which at least one methylene group is replaced by oxygen, C₃-C₂₀ alkenyl, C₃-C₂₀ alkynyl or a group YS; or R¹ and R² can combine on adjacent C-atoms to form a dioxomethylene ring;

R³ signifies C₁-C₂₀ alkyl, C₂-C₂₀ alkyl in which at least one methylene group is replaced by oxygen, C₃-C₂₀ alkenyl, C₃-C₂₀ alkynyl or a group YS;

R⁴, R⁵, R⁶ each independently signify H or C₁-C₂₀ alkyl;

n signifies 0, 1 or 2;

Y signifies a linker group;

S signifies a silane-, an oligosiloxane- or a polysiloxane-moiety;

with the proviso that at least one of the residues R¹, R² or R³ signifies YS.

[0005] The term "C₁-C₂₀ alkyl" refers in the present context to straight chain or branched saturated hydrocarbon residues with 1-20 carbon atoms such as methyl, ethyl, propyl, isopropyl, butyl, sec. butyl, isobutyl, pentyl, neopentyl, hexyl, 2-ethyl-hexyl, octyl and the like.

[0006] The term "C₂-C₂₀ alkyl in which at least one methylene group is replaced by oxygen" refers in the present context to straight chain or branched saturated hydrocarbon residues with up to 19 carbon atoms having at least a group such as -(CH₂-O)-, -(CH₂-CH₂-O)-, -(CH₂-CH₂-CH₂-CH₂-O) and the like.

[0007] The term "C₃-C₂₀ alkenyl" refers in this context to straight chain or branched unsaturated hydrocarbon residues with 3-20 carbon atoms containing a double bond such as propen-2-yl, propen-3-yl, buten-3-yl, buten-4-yl, penten-4-yl, penten-5-yl and the like.

[0008] The term "C₃-C₂₀ alkynyl" refers in this context to straight chain or branched unsaturated hydrocarbon residues with 3-20 carbon atoms containing a triple bond such as propargyl and the like.

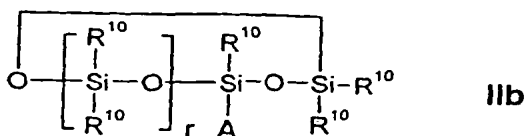
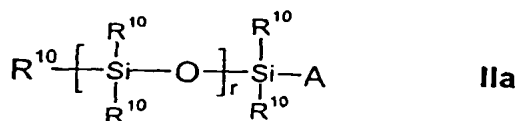
[0009] The term "linker group" refers in this context to a C₃-C₁₂ divalent alkylene or alkenylene chain which links

the silane, oligosiloxane or polysiloxane moiety to the UV absorbing chromophoric residue. The term "C₃-C₁₂ divalent alkylene chain" embraces straight chain or branched saturated hydrocarbon residues such as 3-propylene, 2-propylene, 2-methyl-3-propylene, 3-butylene, 4-butylene, 4-pentylene, 5-pentylene, 6-hexylene and the like. The term "C₃-C₁₂ divalent alkenylene chain" embraces unsaturated hydrocarbon residues containing one or multiple double bonds such as 2-propen-2-ylen, 2-propen-3-ylen, 3-buten-3-ylen, 3-buten-4-ylen, 4-penten-4-ylen, 4-penten-5-ylen, (3-methyl)-penta-2,4-dien-4 or 5-ylen, 11-dodecen-11-ylen and the like. The chains may be interrupted by one or several oxygen atoms forming groups such as 2-ethyloxy-eth-2-ylen, 4-butyloxy-eth-2-ylen, 3,6-dioxa-8-octylene and the like. Preferred linker groups are: 3-propylene, 4-butylene, 2-propen-2-ylen, 2-propen-3-ylen or 3-buten-4-ylen.

[0010] The term "silane" refers in this context to a group -SiR⁷R⁸R⁹ wherein R⁷, R⁸ and R⁹ each independently signify C₁-C₆ alkyl, C₁-C₆ alkoxy or phenyl.

[0011] "C₁-C₆ alkyl" and "C₁-C₆ alkoxy" residues can be straight-chain or branched, such as e.g. methyl, ethyl, propyl, isopropyl, n-butyl, tert.butyl, thexyl, (1,1,2 dimethylpropyl) and, respectively, methoxy, ethoxy, propoxy, isopropoxy, n-butoxy, tert.butoxy, thexoxy. Preferred are alkyl-silane groups such as trimethylsilane, triethylsilane, tripropylsilane, triisopropylsilane, dimethyl tert.butylsilane, dimethyl thexylsilane, triphenylsilane, dimethylphenylsilane and the like.

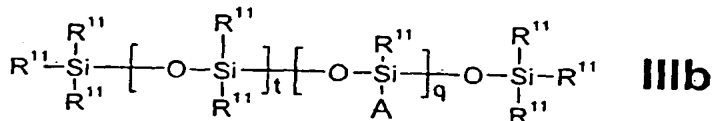
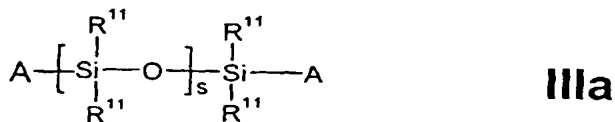
[0012] The term "oligosiloxane" refers in this context to groups of the general formula $\text{SiR}^{10}_m(\text{OSiR}^{10}_3)_n$ with m = 0, 1 or 2; n = 3, 2 or 1 and m+n=3; or groups of the general formula IIa or IIb



wherein

A signifies a bond to the linker Y;
R¹⁰ signifies C₁-C₆ alkyl or phenyl;
r signifies 1 to 9.

[0013] The term "polysiloxane" refers in this context to groups of the general formulae IIIa or IIIb,



wherein

A is a bond to the linker Y;
R¹¹ signifies C₁-C₆ alkyl or phenyl;
s has a value of from 4 to 250;

t has a value of from 5 to 250;

q has a value of from 1 to 30.

[0014] The residues R^1 and R^2 are preferably C_1 - C_6 alkyl, more preferably C_1 - C_4 alkyl, most preferably methyl, or a group YS.

[0015] The residue R^3 is preferably C_1 - C_6 alkyl, more preferably C_1 - C_4 alkyl, most preferably ethyl, or a group YS.

[0016] The residues R^4 and R^5 are preferably C_1 - C_6 alkyl, more preferably C_1 - C_4 alkyl, most preferably methyl.

[0017] The residue R^6 is preferably C_1 - C_6 alkyl, more preferably C_1 - C_4 alkyl, most preferably methyl, or hydrogen.

[0018] The residues R^{10} and R^{11} are preferably C_1 - C_6 alkyl, more preferably C_1 - C_4 alkyl, most preferably methyl.

[0019] The value of "n" is preferably 0 or 1.

[0020] The value of "r" is preferably 1 to 3.

[0021] The value of "s" is preferably 5 to 150.

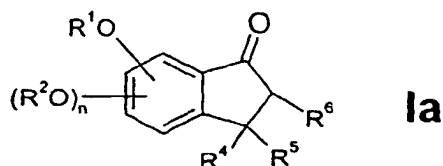
[0022] The value of "q" is preferably 2 to 10, more preferably a statistical mean value of about 4.

[0023] The value of "t" is preferably 5 to 150, more preferably a statistical mean value of about 60.

[0024] Each group R^1 , R^2 or R^3 can signify YS. Thus, the silane-, oligosiloxane- or polysiloxane moiety can be linked via Y to the indane ring or to the carboxy or amid group. Preferably the silane-, oligosiloxane- or polysiloxane moiety is linked to the carboxy or amid group (R^3 is YS).

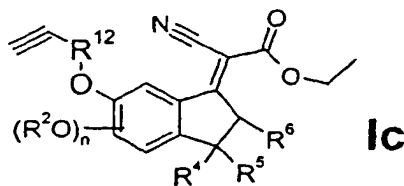
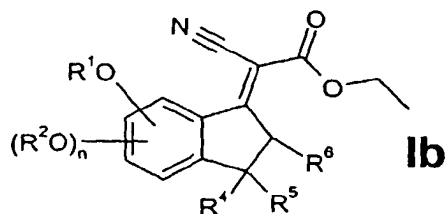
[0025] The compounds of the general formula I can be prepared as follows:

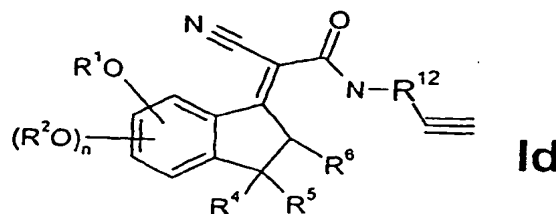
[0026] In a first step compounds of the general formula Ia



wherein R^1 , R^2 , R^4 , R^5 , R^6 and n are as defined above are build up according to known reactions (F. Camps, Z. Naturforsch., B : Anorg. Chem., Org. Chem. (1984), 39B (12), 1801-5), Tetrahedron Letters 27, 2941 (1973).

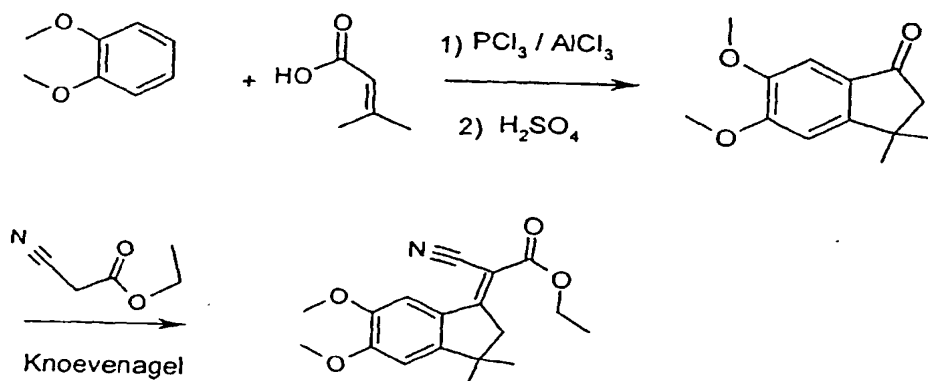
[0027] In a second step indanylidene compounds of the general formulae Ib, Ic and Id



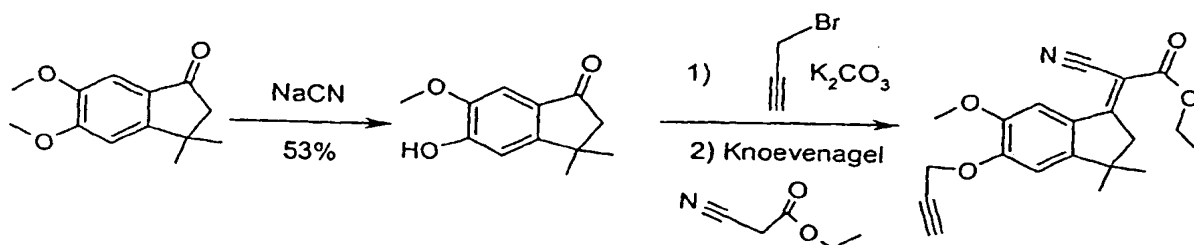


wherein R^1 , R^2 , R^4 , R^5 , R^6 and n are as defined above and R^{12} is a C_3 - C_{12} divalent alkylene- or alkenylene chain are build up according to known reactions such as the Knoevenagel reaction. As stated above the C_3 - C_{12} divalent alkylene- or alkenylene chain may be interrupted by one or several oxygen atoms.

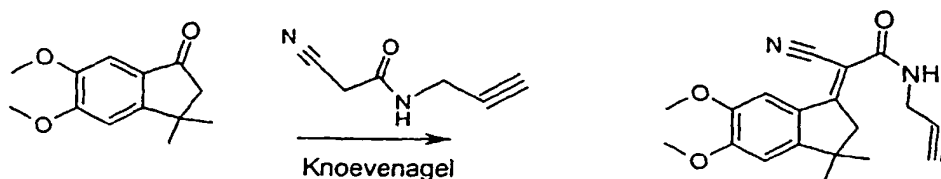
15 [0028] An example to build up an indanylidene compound of the general formula Ib is given below for a compound wherein R^1 and R^2 are methyl, n is 1, R^4 and R^5 are methyl, R^6 is hydrogen and X is oxygen. The corresponding compounds wherein R^1 , R^2 , R^4 , R^5 , R^6 and n are as defined above can be prepared accordingly. The details are described in Example 1.



35 [0029] An example to build up an indanylidene compound of the general formula Ic is given below for a compound wherein R^2 is methyl, n is 1, R^4 and R^5 are methyl, R^6 is hydrogen and X is oxygen. The corresponding compounds wherein R^2 , R^4 , R^5 , R^6 and n are as defined above can be prepared accordingly. The details are described in Examples 11a and 11b.

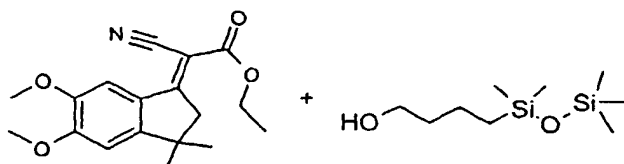


55 [0030] An example to build up an indanylidene compound of the general formula Id is given below for a compound wherein R^1 and R^2 are methyl, n is 1, R^4 and R^5 are methyl, R^6 is hydrogen and X is nitrogen. The corresponding compounds wherein R^1 , R^2 , R^4 , R^5 , R^6 and n are as defined above can be prepared accordingly. The details are described in Examples 8a and 8b.



[0031] In a third step the indanylidene compounds of the general formulae Ib, Ic and Id are linked to the group YS according to known reactions either via a transesterification or a hydrosilation reaction.

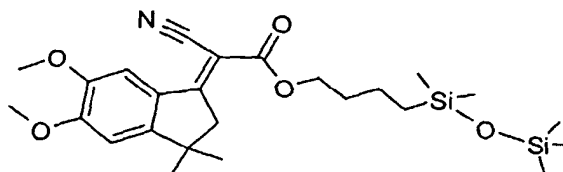
15 [0032] An example for a transesterification reaction is given below for the reaction between a compound of the formula Ib wherein X is oxygen, R¹ and R² are methyl, n is 1, R⁴ and R⁵ are methyl, R⁶ is hydrogen and a compound ZYS, wherein Z is hydroxy, Y is 4-butyl and S is an oligosiloxane of the formula IIa wherein R¹⁰ is methyl and r is 1. The details are described in Example 2. The corresponding compounds of the general formula I wherein X is oxygen e.g. Examples 3-7 can be prepared accordingly.



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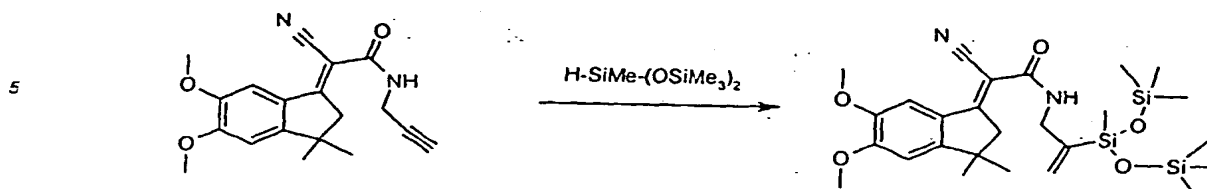
Ti(O-Isoprop)₄



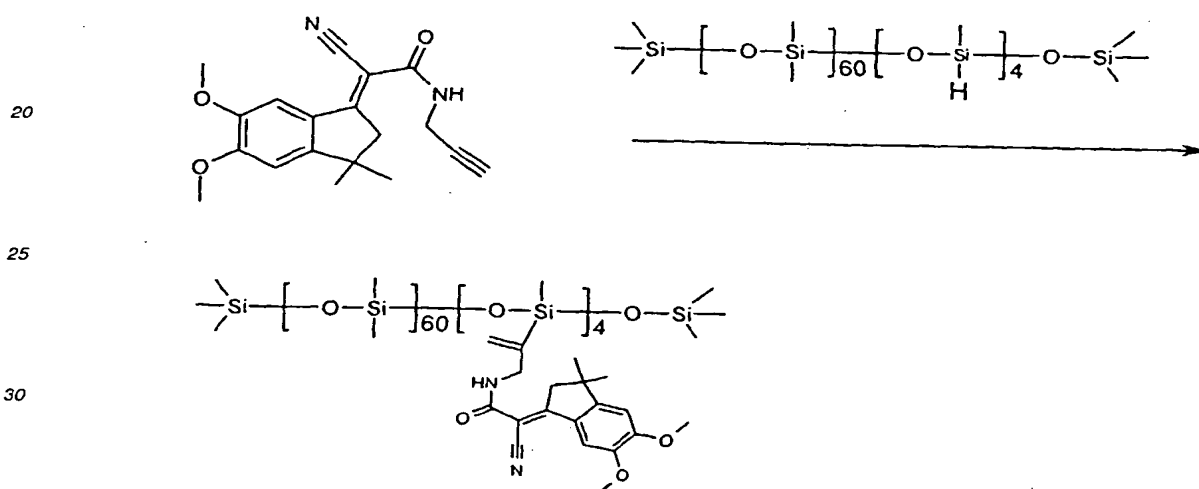
[0033] In the hydrosilation reaction compounds of the general formulae Ic and Id are reacted with a SiH containing oligosiloxane- or polysiloxane compound corresponding to the oligosiloxane- or polysiloxane residues as defined above.

45 [0034] Two examples for a hydrosilation reaction are given below for the reaction between a compound of the formula Id and a SiH containing oligosiloxane and polysiloxane compound respectively. The details are described in Examples 8, 9 and 10. Corresponding compounds of the general formula I wherein X is nitrogen and R³ is YS can be prepared accordingly.

50 a) Hydrosilation according to Example 8



b) Hydrosilation according to Example 9



[0035] Examples 11 and 12 describe the hydrolisation reaction between a compound of the general formula Ic and a SiH containing oligosiloxane- and polysiloxane compound respectively. Compounds of the general formula I wherein X is nitrogen and R¹ is YS can be prepared accordingly.

[0036] The preparation of novel light screening agents, especially of preparations for skin protection and, respectively, sunscreen preparations for everyday cosmetics, comprises incorporating a compound of formula I in a cosmetic base which is usual for light screening agents. Where convenient, other conventional UV-A, and respectively, UV-B filters can also be combined during this incorporation. Said combinations of UV filters can show a synergistic effect. The preparation of said light screening agents is well known to the skilled artisan in this field. The amount of compounds of the general formula I and other known UV-filters is not critical. Suitable amounts are about 0.5 to about 12%.

[0037] Suitable UV B filters, i.e. substances having absorption maxima between about 290 and 320 nm, are for example the following organic compounds which belong to the widest classes of substance:

- 50
- p-Aminobenzoic acid derivatives such as ethyl, propyl, butyl, isobutyl, octyldimethyl, amyldimethyl, ethoxylated ethyl, propoxylated ethylglyceryl or ethylglycosyl p-aminobenzoate and the like;
 - Acrylates such as 2-ethylhexyl 2-cyano-3,3-diphenylacrylate (octocrylene), ethyl 2-cyano-3,3-diphenylacrylate and the like;
 - Aniline derivatives such as methyl anilinum methosulfate and the like;

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 - Anthranilic acid derivatives such as menthyl anthranilate and the like;
 - Benzophenone derivatives such as benzophenone-1 to benzophenone-12 and the like.
 - Camphor derivatives such as methyl benzylidene camphor, 3-benzylidene camphor, camphor benzalkonium methosulfate, polyacrylamidomethyl benzylidene camphor, sulfo benzylidene camphor, sulfomethylbenzylidene

camphor, therephthalidene dicamphor sulfonic acid and the like;

--- Cinnamate derivatives such as octyl methoxycinnamate or ethoxyethyl methoxycinnamate, diethanolamine methoxycinnamate, isoamyl methoxycinnamate and the like as well as cinnamic acid derivatives bond to siloxanes;

--- Gallic acid such as digalloyl trioleate and the like;

--- Imidazole derivatives such as e.g. phenyl benzimidazole sulfonic acid and their salts;

--- Salicylate derivatives such as isopropylbenzyl, benzyl, butyl, octyl, isooctyl or homomenthyl salicylate and the like;

--- Triazole derivatives such as drometriazole, hydroxydibutylphenyl-, hydroxydiamylphenyl-, hydroxyoctylphenyl- or hydroxyphenylbenztriazole and the like;

--- Triazone derivatives such as octyl triazone, dioctyl butamidotriazone and the like; and

--- Pigments such as e.g. microparticulated TiO_2 .

[0038] The formulation may further contain UV-A filters such as

--- Dibenzoylmethane derivatives such as 4-tert. butyl-4'-methoxydibenzoyl-methane and the like;

--- Pigments such as e.g. microparticulated ZnO .

--- Triazine compounds as described in the European Patent Publications EP 0693483 A1, EP 0704437 A2, EP 0704444 A1 and EP 0780382 A1;

---Organosiloxane compounds as described in the European Patent Publications EP 0538431 B1, EP 0709080 A1 and EP 0358584B1;

---Malonates such as described in the European Patent Publication EP 895776 A2.

[0039] The term "microparticulated" refers to a particle size from about 5 nm to about 200 nm, particularly from about 15 nm to about 100 nm.

[0040] As cosmetic bases usual for light screening compositions in the scope of the present invention there can be used any conventional preparation which corresponds to the cosmetic requirements, e.g. creams, lotions, emulsions, salves, gels, solutions, sprays, sticks and milks; see also, Sunscreens, Development, Evaluation and Regulatory Aspects, ed. N.Y. Lowe, N.A. Shaath, Marcel Dekker, Inc. New York and Basel, 1990.

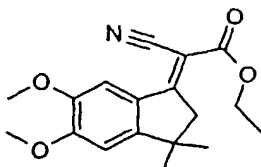
[0041] Having regard to their good lipophilicity, the compounds of the general formula I can be incorporated well into oil containing and fat containing cosmetic preparations such as e.g. in cosmetic preparations containing dimethicone.

[0042] The following examples illustrate the invention in more detail, but do not limit its scope in any manner.

Example 1:

Cyano-(2,3-dihydro-5,6-dimethoxy-3,3-dimethyl-1H-inden-1-ylidene) acetic acid ethyl ester

[0043]

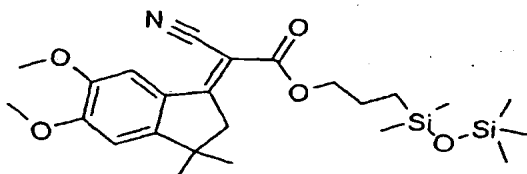


[0044] 122 g (0.55 mol) of 2,3-Dihydro-5,6-dimethoxy-3,3-dimethyl-1H-inden-1-one (CAS N°[4136-26-9] for preparation see F. Camps, Z. Naturforsch., B : Anorg. Chem., Org. Chem. (1984), 39B (12), 1801-5), 63,3 g (0.56 mol) of ethyl cyano acetate, 12 g (0.14 mol) of piperidine, 12 g (0.1 mol) of benzoic acid and 1000 ml toluene were mixed together and heated under reflux for 48 hours. The reaction mixture was cooled to room temperature, washed with diluted HCl, aq Na_2CO_3 , water and dried (MgSO_4). Removal of the solvent and crystallization from EtOH gave 123.8 g of a yellow solid (m.p.:148-149°C). Yield: 71% ; $\epsilon^{1\%}_{1\text{cm}}$: 790 (1 max. : 367 nm) in EtOH. Solubility: 0.35% in Cétol LC

Example 2:

Cyano-(2,3-dihydro-5,6-dimethoxy-3,3-dimethyl-1H-inden-1-ylidene) acetic acid-3-(1,1,3,3,3-pentamethy-disiloxanyl)-propyl ester

[0045]



a) 3-(1,1,3,3,3-Pentamethy-disiloxanyl)-propanol

[0046] A 50 ml reaction flask was charged with 13.6 ml (200 mmol) of allylic alcohol and a catalytic amount of divinyl-tetramethyl disiloxane platinum complex under inert atmosphere and heated to 60°C. 19.5 ml (100mmol) of pentamethyl disiloxane was slowly added through a dropping funnel. The exothermic reaction mixture was stirred over night at 75°C, followed by a distillation at 105 to 107°C / 40 to 41 mbar over a Vigreux column. Yield 18.3 g (88.5% of the theory) of a clear liquid.

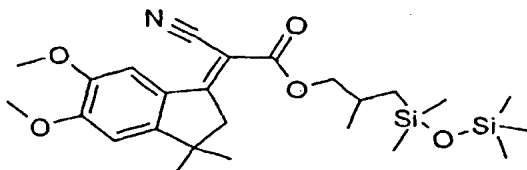
b) Transesterification

[0047] A 25 ml reaction flask equipped with a distillation bridge and connected to vacuum was charged with 2 g (6.3 mmol) of cyano-(2,3-dihydro-5,6-dimethoxy-3,3-dimethyl-1H-inden-1-ylidene) acetic acid ethyl ester (see Example 1), 1.37 g (6.6 mmol) of 3-(1,1,3,3,3-pentamethy-disiloxanyl)-propanol (see above) and 3 mg of tetraisopropyl ortho titanate. The mixture was heated to 115 to 120°C at a vacuum of 360 mbar with stirring for 11 hours. The excess of silylated alcohol was removed at 100°C / 0.2 mbar and the residual product was chromatographed over SiO₂ in hexane : ethylacetate (9.1 to 8:2) to yield 1.2 g (41%) of a liquid honey (m.p.: ca. 25°C), UV 364 nm ($\epsilon=26'093$), which showed excellent solubility in cosmetic solvents such as >20% in Cétiol LC (Coco-caprylate/caprate) and was miscible in Crodamol DA (Diisopropyl adipate). The product showed an excellent photostability in high dilution of an ethanol solution using a Hg-lamp 150 W from Heraeus with Pyrex filter.

Example 3:

Cyano-(2,3-dihydro-5,6-dimethoxy-3,3-dimethyl-1H-inden-1-ylidene) acetic acid-3-(1,1,3,3,3-pentamethy-disiloxanyl)-2-methyl-propyl ester

[0048]



a) 3-(1,1,3,3,3-Pentamethy-disiloxanyl)-2-methyl propanol

[0049] The reaction of Example 2a was repeated using 2-methylalcohol instead of allyl alcohol. After distillation at 105°C / 40 x 10² Pa, 81% of a clear liquid product was obtained.

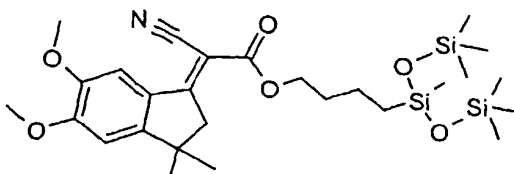
b) Transesterification

[0050] The reaction of Example 2b was repeated using 3-(1,1,3,3,3-pentamethy-disiloxanyl)-2-methyl propanol (see above) instead of 3-(1,1,3,3,3-pentamethy-disiloxanyl)-propanol. After 15 hours reaction time the product was concentrated and chromatographed as above to yield 57% of a liquid material. UV 364 nm (ϵ =25'200), having the same solubility and photostability qualities as described in Example 2b.

Example 4:

Cyano-(2,3-dihydro-5,6-dimethoxy-3,3-dimethyl-1H-inden-1-ylidene) acetic acid-4-(1,3,3,3-tetramethyl-1-[(trimethyl silyl)-oxy]-disiloxanyl)-butyl ester

[0051]



a) 4-(1,3,3,3-Tetramethyl-1-[(trimethyl silyl)-oxy]-disiloxanyl)-butanol

[0052] The reaction of Example 2a was repeated using 1,1,1,3,5,5,5-heptamethyl trisiloxane instead of 1,1,3,3,3-pentamethyl disiloxane and 3-butenol instead of allyl alcohol. After distillation at 78°C / 0.1 x 10² Pa, 83% of a clear liquid product was obtained.

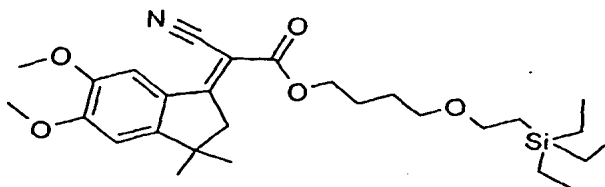
b) Transesterification

[0053] A 25 ml reaction flask equipped with a distillation bridge and connected to vacuum was charged with 1.67 g (5.3 mmol) of Cyano-(2,3-dihydro-5,6-dimethoxy-3,3-dimethyl - 1H-inden-1-ylidene) acetic acid ethyl ester (see example 1), 1.64 g (5.6 mmol) of 4-(1,3,3,3-tetramethyl-1-[(trimethyl silyl)-oxy]-disiloxanyl)-butanol (see above) and 3 mg of tetraisopropyl ortho titanate. The mixture was heated to 125°C at a vacuum of 270 mbar under stirring for 9 hours. The excess of silylated alcohol was removed at 0.2 mbar and the residual product was chromatographed over SiO₂ in hexane : ethylacetate (9.1 to 7:3) to yield 2.3 g (78%) of a liquid, UV 364 nm (ϵ =25'800) and 376 nm (ϵ =25'180). The product was miscible in Cétiol LC and Crodamol DA and showed an excellent photostability in high dilution of an ethanol solution using a Hg-lamp 150 W from Heraeus with Pyrex filter.

Example 5:

Cyano-(2,3-dihydro-5,6-dimethoxy-3,3-dimethyl-1H-inden-1-ylidene) acetic acid-4-(2-triethylsilyl-ethoxy)-butyl ester

[0054]



a) 4-(2-Triethylsilyl-ethoxy)-butanol

[0055] A 50 ml reaction flask was charged with 11.6 ml (100 mmol) of 1,4-butanediol-mono vinylether and a catalytic amount of divinyl-tetramethyl disiloxane platinum complex under inert atmosphere and heated to 60°C. 10.4 g (90 mmol) of triethylsilane was slowly added through a dropping funnel. The exothermic reaction mixture was stirred at 75°C for 18 hours, followed by distillation at 105 to 107°C / 0.2 mbar over a 10 cm Vigreux column. Yield 15.2 g (66% of the theory) of a clear liquid. Purity: 98.7% according to gas chromatography.

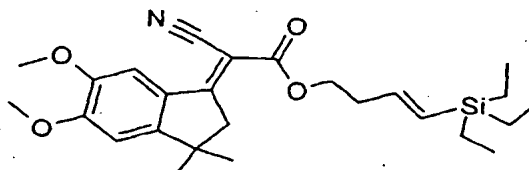
b) Transesterification

[0056] The reaction of Example 2b was repeated using 4-(2-triethylsilyl-ethoxy)-butanol (see above) instead of 3-(1,1,3,3,3-pentamethyl-disiloxanyl)-propanol. After 8 hours reaction time the product was concentrated and chromatographed as above to yield 70% of a liquid material. UV 364 nm ($\epsilon=27'126$), having the same solubility and photostability qualities as described in Example 2b.

Example 6:

Cyano-(2,3-dihydro-5,6-dimethoxy-3,3-dimethyl-1H-inden-1-ylidene) acetic acid-4-triethylsilyl-but-3-enyl ester

[0057]



a) 4-Triethylsilyl-1-but-3-enol

[0058] A 50 ml reaction flask was charged with 1-butyne-3-ol and a catalytic amount of bis(1,5-cyclooctadiene)-di-Rh(I)-dichloride and triphenylphosphine under inert atmosphere. Triethylsilane was slowly added through a dropping funnel. The reaction mixture was stirred at room temperature for 72 h and then concentrated at the rotary evaporator. The product was chromatographed through SiO₂ in hexane : ethylacetate (95:5 to 70:30) to yield 86% of a yellow liquid. Purity according to gas chromatography: 96% trans and 3.4% cis product.

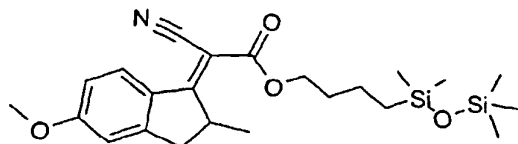
b) Transesterification

[0059] The reaction of Example 2b was repeated using 4-triethylsilanyl-1-but-3-enol (see above) instead of 3-(1,1,3,3,3-pentamethy-disiloxanyl)-propanol. After 9 hours reaction time the product was concentrated and chromatographed as above to yield 65% of a semi-crystalline material. UV 368 nm ($\epsilon=26'748$), having the same solubility and photostability qualities as described in Example 2b.

Example 7:

Cyano-(2,3-dihydro-5-methoxy-2-methyl-1H-inden-1-ylidene) acetic acid-4-(1,1,3,3,3-pentamethy-disiloxanyl)-butyl ester

[0060]



a) 4-(1,1,3,3,3-Pentamethy-disiloxanyl)-butanol

[0061] b) A 50 ml reaction flask was charged with 10.3 ml of 3-butene-1-ol and a catalytic amount of divinyl-tetramethyl disiloxane platinum complex under inert atmosphere and heated to 60°C. 19.5 ml of pentamethyl disiloxane was slowly added through a dropping funnel. The reaction mixture was stirred at 75 to 80°C for three hours, followed by distillation at 110 to 115°C / 38×10^2 Pa over a 10 cm column. Yield: 18.9 g (86% of the theory) of a clear liquid.

c) 2,3-Dihydro-5-methoxy-2-methyl-1H-inden-1-one

[0062] 5-Methoxy indanone was treated with aqueous formaldehyde in the presence of iron pentacarbonyl and KOH in ethanol according to G. Cainelli et. al., *Tetrahedron Letters* 27, 2491 (1973). After chromatography (hexane: ethylacetate = 7:3) over SiO_2 44% yield of white crystals are obtained (m.p. 73-76°C).

c) Cyano-(2,3-dihydro-5-methoxy-2-methyl-1H-inden-1-ylidene) acetic acid 2-ethyl-hexyl ester

[0063] The above 2,3-dihydro-5-methoxy-2-methyl-1H-inden-1-one (5.2 g) was reacted with 5.9 g of 2-ethyl-hexyl cyano acetate in the presence of catalytic amounts of pyrrolidine and benzoic acid in 100 ml of toluene. The reaction mixture was refluxed for 30 hours with simultaneous separation of water. Then the cold reaction mixture was washed with water, concentrated and chromatographed in toluene containing 2% of propanol through SiO_2 to yield 2.6 g of a yellow liquid. UV 347 nm ($\epsilon=33'450$), MS: 355(M^+), 243 (100%), 226, 198.

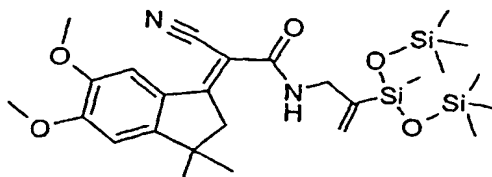
d) Transesterification

[0064] The reaction of Example 2b was repeated using 4-(1,1,3,3,3-pentamethy-disiloxanyl)-butanol (see above) instead of 3-(1,1,3,3,3-pentamethy-disiloxanyl)-propanol as well as the above cyano-(2,3-dihydro-5-methoxy-2-methyl-1H-inden-1-ylidene) acetic acid 2-ethyl-hexyl ester instead of the product of example 1. After 9 hours reaction time the product was concentrated and then treated again for 5 hours as above with new 3-(1,1,3,3,3-pentamethy-disiloxanyl)-propanol. Now the mixture was concentrated and chromatographed as before to yield 30% of a liquid material. UV 347 nm ($\epsilon=32'500$), having the same solubility and photostability qualities as described in Example 2b.

Example 8:

Cyano-(2,3-dihydro-5,6-dimethoxy-3,3-dimethyl-1H-inden-1-ylidene) acetic acid-2-(1,3,3,3-tetramethyl-1-[(trimethylsilyl)-oxy]-disiloxanyl)-prop-2-enyl amide

[0065]



a) 2-Cyano-N-prop-2-ynyl-acetamide

[0066] A mixture of 15.4 ml (240 mmol) of propargyl amine and 17.1 ml (160 mmol) of ethyl cyano acetate was heated for 7 hours to 40°C in a reaction flask. The crystalline material formed was heated further for 17 hours to 70°C. Then the cooled reddish product was dried at high vacuum to yield 18.4 g (94%) of a red powder, m.p. 100-103°C.

b) 2-Cyano-2-(5,6-dimethoxy-3,3-dimethyl-indan-1-ylidene)-N-prop-2-ynyl-acetamide

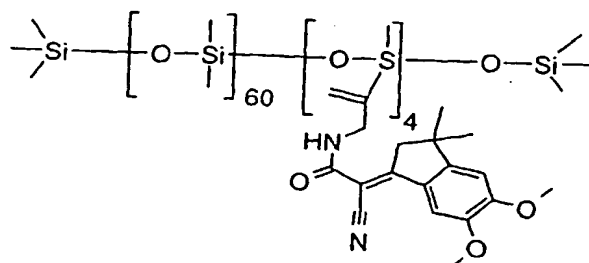
[0067] In a 50 ml reaction flask equipped with a water separator and a reflux condenser was charged with 2.2 g of 2,3-dihydro-5,6-dimethoxy-3,3-dimethyl-1H-inden-1-one (see Example 1) and 1.2 g of 2-cyano-N-prop-2-ynyl-acetamide (see above), catalytic amounts of pyrrolidine and benzoic acid in 20 ml of toluene. The reaction mixture was refluxed for 24 hours with simultaneous separation of water. Then the product in the cold reaction mixture was filtered off and recrystallized in ethylacetate to yield 1.13 g of white crystals, m.p. 202-205°C. UV 362 nm ($\epsilon=24'992$). Solubility : 0.04% in Cétol LC

c) Hydrosilylation reaction

[0068] The above 2-cyano-2-(5,6-dimethoxy-3,3-dimethyl-indan-1-ylidene)-N-prop-2-ynyl-acetamide (320 mg), 220 mg of 1,1,1,3,5,5,5-heptamethyl trisiloxane and a catalytic amount of divinyl-tetramethyl disiloxane platinum complex in 10 ml of toluene was placed in a three-necked reaction flask under inert atmosphere and stirred for 48 hours at 95°C. The product solution is washed with a mixture of water/methanol = 1:10 and concentrated to yield 550 mg (100%) of a yellow liquid. UV 360 nm ($\epsilon=22'069$), MS: 546 (M^+), 531, 299, 270, 269 (100%). Its NMR shows a mixture of the vicinal and the geminal hydrosilylation product of 1:2. The product was miscible in CETIOL LC and CRODAMOL DA and showed the same photostability qualities as described in Example 2b.

Example 9

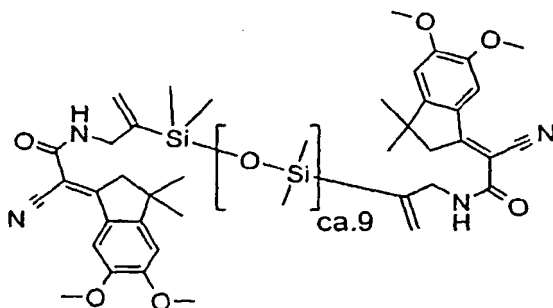
[0069] A polysiloxane which corresponds in its statistical mean value to the following formula:



[0070] 2-Cyano-2-(5,6-dimethoxy-3,3-dimethyl-indan-1-ylidene)-N-prop-2-ynyl-acetamide (320 mg), 1180mg of polysiloxane Ae-151 of Wacker-Chemie GmbH. and a catalytic amount of divinyl-tetramethyl disiloxane platinum complex in 10 ml of toluene was placed in a three-necked reaction flask under inert atmosphere and heated for 48 hours to 95°C. The product solution was washed with a mixture of water/methanol = 1:10 and concentrated to yield 1500 mg (100%) of a yellow liquid. UV 360 nm (E=210.6). The product was miscible in CETIOL LC and CRODAMOL DA and showed the same photostability qualities as described in Example 2b.

Example 10

[0071] α -(Dimethyl-[2N-[2-cyano-2-(5,6-dimethoxy-3,3-dimethyl-indan-1-ylidene)-acetamide]-1-methylene-ethyl]- ω -(dimethyl-[2N-[2-cyano-2-(5,6-dimethoxy-3,3-dimethyl-indan-1-ylidene)-acetamide]-1-methylene-ethyl]-poly-(oxy-(dimethyl)-silene), n ~ 9

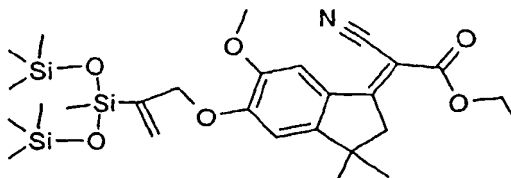


[0072] 2-Cyano-2-(5,6-dimethoxy-3,3-dimethyl-indan-1-ylidene)-N-prop-2-ynyl-acetamide (320 mg), 340 mg of polysiloxane VP-1085 of Wacker-Chemie GmbH. and a catalytic amount of Pt on charcoal 5% in 10 ml of toluene was placed in a three-necked reaction flask under inert atmosphere and heated for 44 hours to 105°C. The product solution was filtered through Cellite, washed with a mixture of water/methanol = 1:10 and concentrated to yield 560 mg (85%) of a yellow liquid. UV 360 nm (E=329). The product was miscible in CETIOL LC and CRODAMOL DA and showed the same photostability qualities as described in Example 2b.

Example 11

Cyano-(6-methoxy-3,3-dimethyl-5-[2-((1,3,3,3-tetramethyl-1-[(trimethyl silyl)-oxy]-disiloxanyl)-allyloxy]-indan-1-ylidene)-acetic acid ethyl ester

[0073]



a) 6-Methoxy-3,3-dimethyl-5-hydroxy-indan-1-one

[0074] In a three necked reaction flask equipped with a reflux condenser, a mixture of 5 g of 2,3-dihydro-5,6-dimethoxy-3,3-dimethyl-1H-inden-1-one (see example 1) and 5.5 g of sodium cyanide in 44.5 ml of dimethyl formamide was

stirred at 100°C for 40 hours. Then the mixture was poured on an aqueous NaH_2PO_4 solution and extracted 4 times with ethyl acetate, dried over Na_2CO_3 and concentrated. The raw product was chromatographed in methylene chloride containing 1% of methanol to yield 2.5 g of white crystals. m.p. 105-107°C. MS: 206(M^+), 191(100%), 163, 131, 103.

5 b) 6-Methoxy-3,3-dimethyl-5-prop-2-ynyloxy-indan-1-one

[0075] 6-Methoxy-3,3-dimethyl-5-hydroxy-indan-1-one (2.2 g), 1.5 g of propargyl bromide and 3.7 g of K_2CO_3 in 9 ml of 1-methyl pyrrolidone was placed in a 25 ml reaction flask and stirred for one hour. Then it was stirred further at 100°C for one hour. The reaction mixture was distributed between water and ethyl acetate. The organic phase was washed with 1n NaOH solution and NaCl solution, dried over Na_2SO_4 and concentrated to yield 2.7 g of a yellow liquid. UV 310 nm ($\epsilon=18'734$), MS: 244(M^+), 229, 105(100%).

c) Cyano-(6-methoxy-3,3-dimethyl-5-prop-2-ynyloxy-indan-1-ylidene)-acetic acid ethyl ester

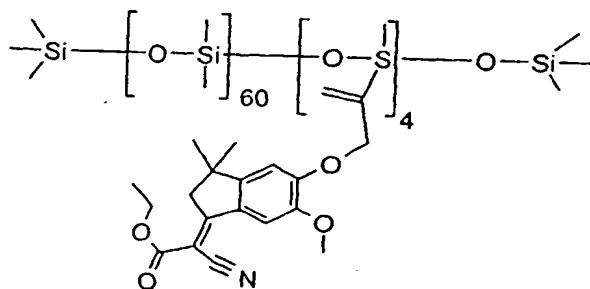
15 [0076] The above 6-methoxy-3,3-dimethyl-5-prop-2-ynyloxy-indan-1-one (2.44 g) was treated with 1.13 g of ethyl cyano acetate in the presence of 0.1 equivalents of pyrrolidine and benzoic acid in 20 ml of xylene. The reaction mixture was refluxed for 30 hours with simultaneous separation of water. Then the cold reaction mixture was washed with water, concentrated and chromatographed in hexane / ethyl acetate through SiO_2 to yield 0.7 g of yellow crystals. m.p. 132-136°C. UV 362 nm ($\epsilon=23'222$), MS: 339(M^+), 324, 300 (100%).

20 d) Hydrosilylation reaction

[0077] Cyano-(6-methoxy-3,3-dimethyl-5-prop-2-ynyloxy-indan-1-ylidene)-acetic acid ethyl ester (500 mg), 330 mg of 1,1,1,3,5,5,5-heptamethyl trisiloxane and a catalytic amount of divinyl-tetramethyl disiloxane platinum complex in 15 ml of toluene was placed in a three-necked reaction flask under inert atmosphere and heated for 24 hours to 78°C. The product solution was concentrated and filtered through SiO_2 in hexane / ethyl acetate = 9:1 and again concentrated to yield 590 mg (71%) of a yellow liquid. UV 367 nm ($\epsilon=23'515$), MS: 561(M^+), 546, 509(100%). Its NMR shows a mixture of the vicinal and the geminal hydrosilylation product of 2:1. The product was miscible in CETIOL LC and CRODAMOL DA and showed the same photostability qualities as described in Example 2b.

30 Example 12

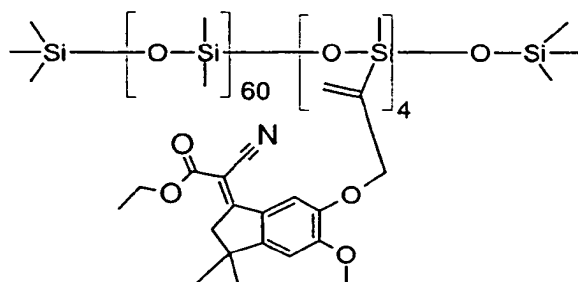
[0078] A polysiloxane which corresponds in its statistical mean value to the following formula:



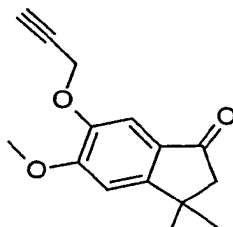
50 [0079] Cyano-(6-methoxy-3,3-dimethyl-5-prop-2-ynyloxy-indan-1-ylidene)-acetic acid ethyl ester (280 mg), 770 mg of polysiloxane Ae-151 of Wacker-Chemie GmbH. and a catalytic amount of divinyl-tetramethyl disiloxane platinum complex in 10 ml of toluene was placed in a three-necked reaction flask under inert atmosphere and heated for 20 hours to 80°C. The product solution was washed with a mixture of water/methanol = 1:10, concentrated and filtered through SiO_2 to yield 1100 mg (100%) of a yellow liquid. UV 366 nm ($\epsilon=26'172$ / E180.5). Its NMR shows both vicinal and geminal hydrosilylation product. The product was miscible in CETIOL LC and CRODAMOL DA and shows the same photostability qualities as described in Example 2b.

Example 13

[0080] A polysiloxane which corresponds in its statistical mean value to the following formula

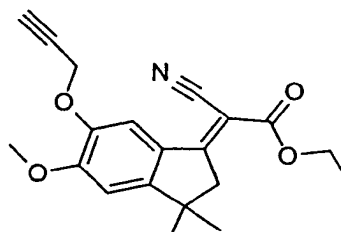


[0081] In a first step 5-methoxy-3,3-dimethyl-6-prop-2-ynyloxy-indan-1-one was prepared as follows:



[0082] 45.8 g of 5-methoxy-3,3-dimethyl-6-hydroxy-indan-1-one (CAS N°[98910-58-8], 24.4 g of propargyl chloride and 8.9 g of NaH in 300 ml of DMF were stirred for one hour at room temperature and then heated for 20 hours at 50 °C. The reaction mixture was distributed between water and toluene. The organic phase was washed with Na₂CO₃ and water, dried over Na₂SO₄ and concentrated to yield 41.7 g of a brown liquid. ¹H-NMR (200 MHz): 1.41 (s, 6H); 2.52-2.58 (m, 3H); 3.99 (s, 3H); 4.79 (d, J= 2 Hz, 2H); 6.89 (s, 1H); 7.27 (s, 1H).

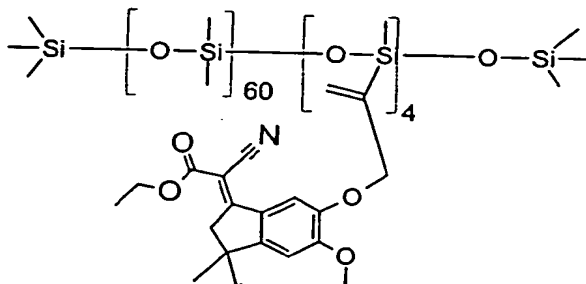
[0083] To prepare cyano-(5-methoxy-3,3-dimethyl-6-prop-2-ynyloxy-indan-1-ylidene)-acetic acid ethyl ester



[0084] 41.7 g of the above 5-methoxy-3,3-dimethyl-6-prop-2-ynyloxy-indan-1-one was treated with 21.49 g of ethyl cyano acetate in the presence of 16 g of piperidine and 16 g of benzoic acid in 1300 ml of cyclohexane. The reaction mixture was refluxed for 24 hours with simultaneous separation of water. Then the cold reaction mixture was washed with water, HCl 1%, Na₂CO₃ and water. The reaction mixture was concentrated and recrystallised in EtOH to yield 24.3 g of yellow crystals. ¹H-NMR (200 MHz): 1.33 (s, 6H); 1.38 (t, J= 7Hz, 3H); 2.57 (t, J= 2 Hz, 1H); 3.37 (s, 3H); 3.99 (s,

3H); 4.31 (q, J= 7Hz, 2H); 4.83 (d, J= 2 Hz, 2H); 6.80 (s, 1H); 8.26 (s, 1H).

[0085] α -(Trimethylsilyl)- ω -(trimethylsilyl-oxy)-poly-(oxy-(dimethyl)- and ca. 7.5% of methyl-(6-[-1-cyano-ethoxy-acetyl-(5-methoxy-3,3-dimethyl-indan-1-ylidene)-1-methylene-eth-2-oxy]-silene)



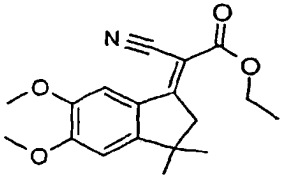
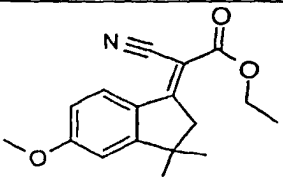
[0086] 16.13 g of the above Cyano-(5-methoxy-3,3-dimethyl-6-prop-2-ynyloxy-indan-1-ylidene)-acetic acid ethyl ester, 54.95 g of polysiloxane Ae-151 of Wacker-Chemie GmbH. and a catalytic amount of Pt/C (Heraeus type k-0101) in 75 ml of toluene were heated for 28 hours at 110°C. The reaction mixture was filtrated and then washed with a mixture of water/methanol = 1:5, concentrated to give 67.8 g a yellow liquid. UV 368 nm (E=150). Its NMR shows both vicinal and geminal hydrosilylation product. The product was miscible in CETIOL LC and CRODAMOL DA and shows the same photostability qualities as described in Example 2b.

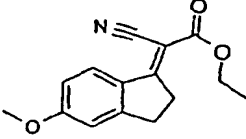
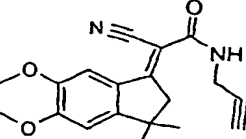
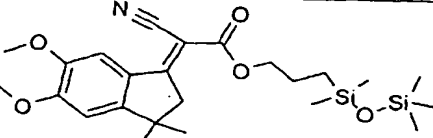
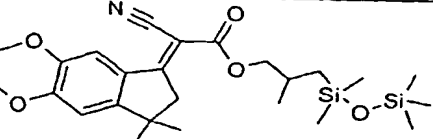
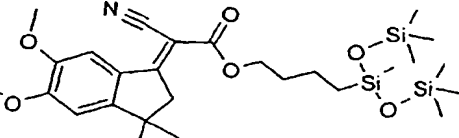
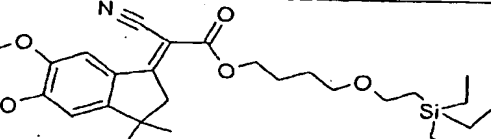
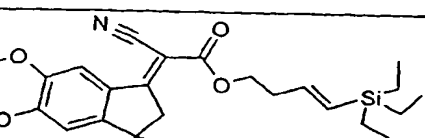
Solubility

[0087] The compounds of the general formula I are excellent soluble in cosmetic solvents. The compounds of Examples 2 to 12 are miscible in CRODAMOL DA. The solubility in CETIOL LC is >20% for compounds of Examples 2, 3, 5 and 6. Examples 4 and 8 to 12 are miscible in CETIOL LC.

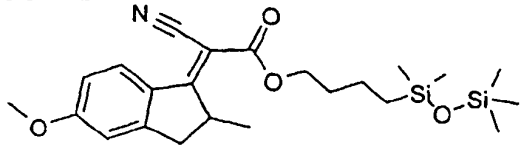
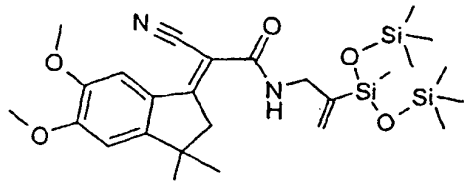
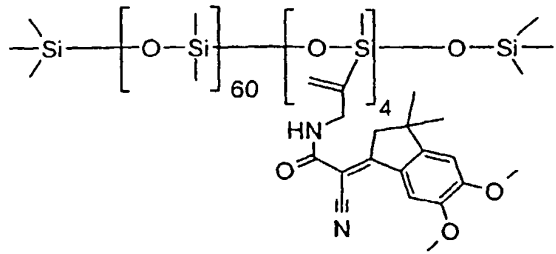
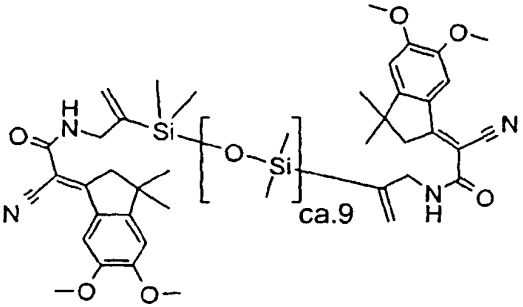
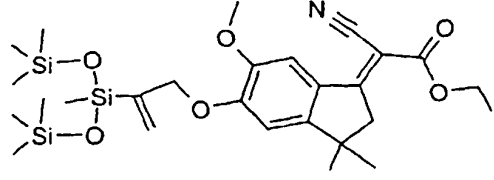
[0088] The following Table 1 shows solubility data of indanylidene compounds disclosed in the European patent publication EP 0823 418 A2 and of compounds according to the invention.

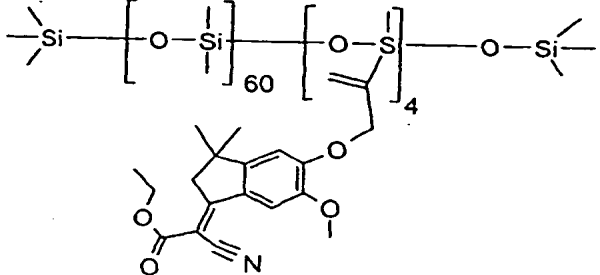
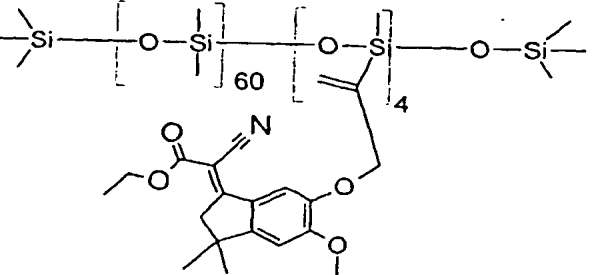
Table 1

Compound	Solubility in CETIOL LC	Solubility in CRODAMOL DA
	0.35%	1.71%
	0.10%	0.60%

5		0.09%	—
10		0.04%	—
15			
20		>20%	miscible
25		>20%	miscible
30			
35		miscible	miscible
40		>20%	miscible
45			
50		>20%	miscible

55

5		miscible	miscible
10		miscible	miscible
15			
20		miscible	miscible
25			
30			
35		miscible	miscible
40			
45		miscible	miscible
50			

	miscible	miscible
	miscible	miscible

The following Examples 14-16 illustrate light screening agents provided by the present invention.
In these examples the trade names selected have the following significance:

- AMPHISOL DEA: Diethanolamine cetylphosphate sold under the tradename AMPHISOL DEA by Givaudan Roure S.A, F-95101 Argenteuil-Paris.
- CARBOPOL 934: Carbomer sold under the tradename CARBOPOL 934 by B.F. Goodrich Company, Brecksville, OH 44141, USA.
- CERAPHYL 375: Isostearyl neopentanoate sold under the tradename CERAPHYL 375 by ISP Global Technologies Deutschland GmbH, Frechen, Germany.
- CERAPHYL 847: Octyldodecyl stearoyl stearate sold under the tradename CERAPHYL 847 by ISP.
- CETIOL LC: Coco-caprylate/caprate sold under the tradename CETIOL LC by Henkel KgA, Düsseldorf, Germany.
- CRODAMOL DA: Diisopropyladipate sold under the tradename CRODAMOL DA by Croda.
- DERMOL 185: Isostearyl neopentanoate sold under the tradename DERMOL 185 by Bernel.
- EDETA BD: Disodium EDTA sold under the tradename EDETA BD by BASF AG, Ludwigshafen, Germany.
- ESTOL GTEH 3609: Trioctanoin sold under the trade name ESTOL GTEH 3609 by Unichema Chemie GmbH, Emmerich, Germany.
- ESTOL GMM 3650: Glyceryl Myristate sold under the trade name ESTOL GMM 3650 by Unichema.
- GANEX V-220: PVP/Eicosene copolymer sold under the tradename GANEX V-220 by ISP.

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NIPAGIN M:	Methylparaben sold under the tradename NIPAGIN M by Nipa Lab. Ltd., Pontypridd Mid Glam, Wales/GB
PARSOL MCX:	Octyl methoxycinnamate sold under the tradename PARSOL MCX by F. Hoffmann-la Roche Ltd, CH-4070 Basel.
PARSOL 1789:	4-t-Butyl-4'-methoxy-dibenzoyl-methane sold under the trade name PARSOL 1789 by Roche.
PARSOL 5000:	4-Methylbenzylidene camphor sold under the tradename PARSOL 5000 by Roche.
PHENONIP:	Phenoxyethanol & Methyl-, Ethyl-, Propyl- & Butyl-paraben sold under the tradename PHENONIP by Nipa.
T-COTE 031:	Titanium Dioxide & Dimethicone sold under the tradename T-COTE 031 by Sunsmart, Wainscott- NY 11975, USA

Example 14

[0091] Preparation of a O/W broad spectrum sunscreen lotion containing 2% of the product described in Example 2.

% w/w	Ingredient	Chemical Name/INCI Name
Part A		
2.0	PARSOL MCX	Octyl methoxycinnamate
2.0	Product of Example 2	
3.0	PARSOL 1789	4-t-Butyl-4'-methoxy-dibenzoyl-methane
12.0	CETIOL LC	Coco-caprylate/caprate
4.0	DERMOL 185	Isostearyl neopentanoate
0.25	Diethyleneglycol monostearate	PEG-2-stearate
1.0	Cetylalcohol	Cetylalcohol
0.25	MPOB/PPOB	Methyl-propylparabene
0.1	EDTA BD	EDTA-sodium salt
1.0	AMPHISOL DEA	Diethanolamine cetylphosphate
Part B		
20.0	Permulene TR-1 (+%)	Acrylate C10-C30 Alkylacrylate
48.6	Deionized Water	Deionized Water
5.0	Propyleneglycol	1,2-Propanediol
0.8	KOH(10%)	Potassium hydroxyde

[0092] Part A was heated in a reactor to 85°C. Part B was slowly added within 10 mm., followed by addition of KOH, cooling and degassing of the emulsion.

Example 15

[0093] Preparation of a O/W anionic broad spectrum sunscreen lotion containing 4% of the product described in Example 8.

% w/w	Ingredient	Chemical Name/INCI Name
Part A		
3.0	PARSOL MCX	Octyl methoxycinnamate
4.0	Product of Example 8	
3.0	PARSOL 5000	4-Methylbenzylidene camphor
4.0	PARSOL 1789	4-t-Butyl-4'-methoxy-dibenzoyl-methane
2.0	Glyceryl monostearate	Glyceryl stearate
2.0	Cetyl alcohol extra	Cetyl alcohol
2.0	GANEX V-220	PVP/Eicosene copolymer
4.0	CERAPHYL 375	Isostearyl neopentanoate
4.0	CERAPHYL 847	Octyldodecyl stearoyl stearate
2.0	AMPHISOL K	Potassium cetylphosphate
0.1	EDETA BD	Disodium EDTA
0.6	PHENONIP	Phenoxyethanol & Methyl-, Ethyl-, Propyl- & Butyl-paraben
Part B		
11.2	Deionized Water	Deionized Water
50.0	CARBOPOL 934 1% solution	Carbomer
5.0	Propyleneglycol	1,2-Propanediol
0.2	NIPAGIN M	Methylparaben
3.0	KOH (10%)	Potassium hydroxyde
q.s.	Perfume oil	Fragrance

[0094] Part A was heated in a reactor to 85°C. When homogeneous Part B was added, followed by addition of pre-heated KOH (75°C), cooling and degassing of the emulsion.

Example 16

[0095] Preparation of a O/W broad spectrum sunscreen cream with pigments having low skin penetration quality and containing 4% of the product described in Example 9.

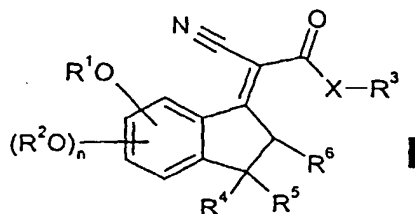
% w/w	Ingredients	Chemical Name/INCI Name
Part A		
8.0	Polysiloxane A described in EP 0709080 A1	Polysiloxane grafted benzalmonate UV-B sunscreen
4.0	Product of Example 9	
6.0	T-COTE 031	Titanium Dioxide & Dimethicone
10.0	ESTOL GTEH 3609	Trioctanoin
1.0	Cetyl Alcohol	Cetyl Alcohol
4.0	ESTOL GMM 3650	Glyceryl Myristate
0.05	Butylated Hydroxytoluene	BHT
0.1	EDETA BD	Disodium EDTA
0.6	PHENONIP	Phenoxyethanol & Methylparaben & Ethylparaben & Propylparaben & Butylparaben
2.0	AMPHISOL K	Potassium Cetyl Phosphate
Part B		
50.8	Deionized Water	Deionized Water
10.0	Carbopol 980 1 % sol'n	Carbomer 980
3.0	Glycerin	Glycerin
Part C		
0.5	KOH 10 % sol'n	Potassium Hydroxide
Part D		
q.s.	Perfume Oil	Fragrance

Procedure

[0096] The ingredients of Part A were heated to 85°C while stirring. After mixing for 30 sec. with a turbine at 8000 t/min. the ingredients of Part B and Part C were added to the homogeneous mixture. The mixture was heated to 75°C, while stirring. After cooling to 40°C the ingredients of Part D were added. The water loss was compensated and the mixture was cooled to room temperature under stirring followed by mixing for 30 sec. with a turbine at 8000 t/min.

Claims

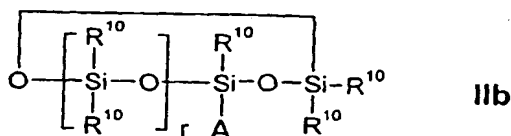
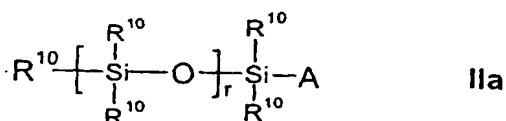
- Compounds of the general formula I



wherein

- X signifies O or NH;
- R¹ signifies C₁-C₂₀ alkyl, C₂-C₂₀ alkyl in which at least one methylene group is replaced by oxygen, C₃-C₂₀ alkenyl, C₃-C₂₀ alkynyl or a group YS;
- R² signifies C₁-C₂₀ alkyl, C₂-C₂₀ alkyl in which at least one methylene group is replaced by oxygen, C₃-C₂₀ alkenyl, C₃-C₂₀ alkynyl or a group YS; or R¹ and R² can combine on adjacent C-atoms to form a dioxomethylene ring;
- R³ signifies C₁-C₂₀ alkyl, C₂-C₂₀ alkyl in which at least one methylene group is replaced by oxygen, C₃-C₂₀ alkenyl, C₃-C₂₀ alkynyl or a group YS;
- R⁴, R⁵, R⁶ each independently signify H or C₁-C₂₀ alkyl;
- n signifies 0, 1 or 2;
- Y signifies a linker group;
- S signifies a silane-, an oligosiloxane- or a polysiloxane-moiety;
- with the proviso that at least one of the residues R¹, R² or R³ signifies YS.

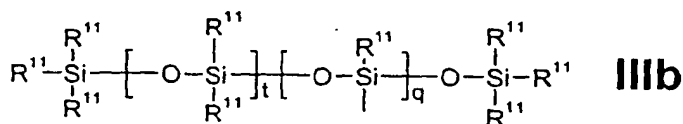
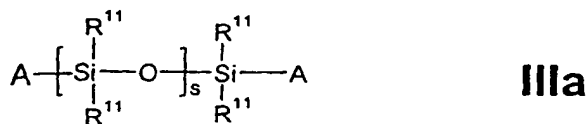
2. Compounds according to claim 1, wherein R² signifies C₁-C₂₀ alkyl, C₂-C₂₀ alkyl in which at least one methylene group is replaced by oxygen, C₃-C₂₀ alkenyl, C₃-C₂₀ alkynyl; or R¹ and R² can combine on adjacent C-atoms to form a dioxomethylene ring.
3. Compounds according to claim 1 or 2, wherein the linker group signifies a C₃-C₁₂ divalent alkylene or alkenylene chain which links the silane, oligosiloxane or polysiloxane moiety to the UV absorbing chromophoric residue.
4. Compounds according to claim 3, wherein the linker group signifies 3-propylene, 2-propylene, 2-methyl-3-propylene, 3-butylene, 4-butylene, 4-pentylene, 5-pentylene, 6-hexylene, 2-propen-2-ylene, 2-propen-3-ylene, 3-buten-3-ylene, 3-buten-4-ylene, 4-penten-4-ylene, 4-penten-5-ylene, (3-methyl)-penta-2,4-dien-4 or 5-ylene, 11-dodecen-11-ylene, 2-ethoxy-eth-2-ylene, 4-butyloxy-eth-2-ylene or 3,6-dioxa-8-octylene.
5. Compounds according to any one of claims 1-4, wherein S signifies a group of the general formula -SiR⁷R⁸R⁹ wherein R⁷, R⁸ and R⁹ each independently signify C₁-C₆ alkyl, C₁-C₆ alkoxy or phenyl.
6. Compounds according to claim 5, wherein S signifies trimethylsilane, triethylsilane, tripropylsilane, triisopropylsilane, dimethyl tert.butylsilane, dimethyl hexylsilane, triphenylsilane, dimethylphenylsilane.
7. Compounds according to any one of claims 1-4, wherein S signifies a group of the general formula -SiR¹⁰_m(OSiR¹⁰₃)_n with m = 0, 1 or 2; n = 3, 2 or 1 and m+n = 3; or groups of the general formula IIa or IIb



wherein

A signifies a bond to the linker Y;
 R^{10} signifies C_1 - C_6 alkyl or phenyl;
 r signifies 1 to 9.

8. Compounds according to any one of claims 1-4, wherein S signifies a polysiloxane group of the general formula IIIa or IIIb,



wherein

A is a bond to the linker Y;
 R^{11} signifies C_1 - C_6 alkyl or phenyl;
 s has a value of from 4 to 250;
 t has a value of from 5 to 250;
 q has a value of from 1 to 30.

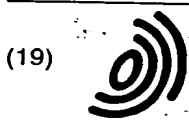
9. Compounds according to any one of claims 1-8, wherein R^1 and R^2 signify C_1 - C_6 alkyl, preferably C_1 - C_4 alkyl, more preferably methyl, or a group YS.
10. Compounds according to any one of claims 1-9, wherein R^3 signifies C_1 - C_6 alkyl, preferably C_1 - C_4 alkyl, more preferably ethyl, or a group YS.
11. Compounds according to anyone of claims 1-10, wherein R^4 and R^5 signify C_1 - C_6 alkyl, preferably C_1 - C_4 alkyl, more preferably methyl.
12. Compounds according to any one of claims 1-11, wherein R^6 signifies C_1 - C_6 alkyl, preferably C_1 - C_4 alkyl, more preferably methyl, or hydrogen.
13. Compounds according to any one of claims 7 and 9-12, wherein R^{10} signifies C_1 - C_6 alkyl, preferably C_1 - C_4 alkyl, more preferably methyl.
14. Compounds according to anyone of claims 7 and 9-13, wherein r is 1 to 3.
15. Compounds according to anyone of claims 8-12, wherein R^{11} signifies C_1 - C_6 alkyl, preferably C_1 - C_4 alkyl, more preferably methyl.
16. Compounds according to any one of claims 8-12 and 15, wherein s is 5 to 150.
17. Compounds according to any one of claims 8-12, 15 and 16, wherein t is 5 to 150, preferably a statistical mean value of about 60.
18. Compounds according to any on of claims 8-12 and 15-17, wherein q is 2 to 10, preferably a statistical mean value of about 4.
19. Compounds according to any one of claims 1-18, wherein n is 0 or 1.

20. Light screening composition comprising a compound according to any one of claims 1-19.

21. Light screening composition according to claim 20, characterized in that it contains, in addition, common UV-A and/or UV-B screening agents.

22. The use of a compound according to any one of claims 1-19 as absorber for the ultraviolet light.

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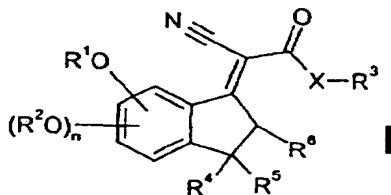
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(54) Novel indanylidene compounds

(57) The invention relates to novel indanylidene compounds which are effective in absorbing ultra violet radiation and to light screening compositions comprising said indanylidene compounds of the general formula I



wherein

- X signifies O or NH;
- R¹ signifies C₁-C₂₀ alkyl, C₂-C₂₀ alkyl in which at least one methylene group is replaced by oxygen, C₃-C₂₀ alkenyl, C₃-C₂₀ alkynyl or a group YS;
- R² signifies C₁-C₂₀ alkyl, C₂-C₂₀ alkyl in which at least one methylene group is replaced by oxygen, C₃-C₂₀ alkenyl, C₃-C₂₀ alkynyl or a group YS; or R¹

and R² can combine on adjacent C-atoms to form a dioxomethylene ring;

R³ signifies C₁-C₂₀ alkyl, C₂-C₂₀ alkyl in which at least one methylene group is replaced by oxygen, C₃-C₂₀ alkenyl, C₃-C₂₀ alkynyl or a group YS;

R⁴, R⁵, R⁶ each independently signify H or C₁-C₂₀ alkyl;

n signifies 0, 1 or 2;

Y signifies a linker group;

S signifies a silane-, an oligosiloxane- or a polysiloxane-moiety;

with the proviso that at least one of the residues R¹, R² or R³ signifies YS.

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EUROPEAN SEARCH REPORT

Application Number
EP 99 12 2210

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Place of search THE HAGUE		Date of completion of the search 23 January 2002	Examiner Bader, K
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 23 January 2002	Examiner: Bader, K
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons * : member of the same patent family, corresponding document</p>			

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Application Number
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			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
The present search report has been drawn up for all claims			
Place of search: THE HAGUE		Date of completion of the search: 23 January 2002	Examiner: Bader, K
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons K : member of the same patent family, corresponding document</p>			

EP 99 12 2210 (99/02/21)

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EP 99 12 2210

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23-01-2002

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